

TITLECHARGE TRANSPORT COMPOSITIONS AND ELECTRONIC
DEVICES MADE WITH SUCH COMPOSITIONSBACKGROUND OF THE INVENTION5 Cross Reference to Related Applications

 This application claims priority from U.S. Provisional Application
Serial No. 60/394767, filed July 10, 2002, and U.S. Provisional Application
Serial No. 60/458277, filed March 28, 2003.

Field of the Invention

10 The present invention relates to charge transport compositions.
The invention further relates to photoactive electronic devices in which
there is at least one active layer comprising such charge transport
compositions.

Background

15 In organic photoactive electronic devices, such as light-emitting
diodes ("OLED"), that make up OLED displays, the organic active layer is
sandwiched between two electrical contact layers in an OLED display. In
an OLED the organic photoactive layer emits light through the light-
transmitting electrical contact layer upon application of a voltage across
20 the electrical contact layers.

 It is well known to use organic electroluminescent compounds as
the active component in light-emitting diodes. Simple organic molecules,
conjugated polymers, and organometallic complexes have been used.

 Devices which use photoactive materials, frequently include one or
25 more charge transport layers, which are positioned between the
photoactive (e.g., light-emitting layer) layer and one of the contact layers.
A hole transport layer may be positioned between the photoactive layer
and the hole-injecting contact layer, also called the anode. An electron
transport layer may be positioned between the photoactive layer, such as
30 the organometallic light emitting material, in photoactive devices, and the
electron-injecting contact layer, also called the cathode.

 There is a continuing need for charge transport materials and anti-
quenching materials.

SUMMARY OF THE INVENTION

35 The present invention is directed to a charge transport composition
which is a quinoxaline derivative. The quinoxaline derivative has Formula
I, shown in Figure 1, wherein:

R¹ and R² are the same or different at each occurrence and are selected from H, F, Cl, Br, hydroxyl, carboxyl, carbonyl, silyl, siloxyl, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, C_nH_aF_b, OC_nH_aF_b, C₆H_cF_d, and OC₆H_cF_d, or both of R² together may constitute an arylene or heteroarylene group;

a, b, c, and d are 0 or an integer such that a+b = 2n + 1, and c + d = 5,

n is an integer from 1 through 12; and

z is 0 or an integer from 1 through 4.

In another embodiment, the present invention is directed to a charge transport composition having Formula II, shown in Figure 2, wherein:

R¹, R², a through d and n are as defined above,

R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene; alkynylene, alkynylenearylene, alkynyleneheteroarylene.

Q is selected from a single bond and a multivalent group;

m is an integer equal to at least 2,

p is 0 or 1 and

x is 0 or an integer from 1 to 3.

In another embodiment, the present invention is directed to a charge transport composition having Formula III, shown in Figure 3, wherein:

R¹, R², a through d, n, and z are as defined above,

R³ is the same or different at each occurrence and is selected from a single bond and a group selected from alkylene, heteroalkylene, arylene, heteroarylene, arylenealkylene, and heteroarylenealkylene; alkynylene, alkynylenearylene, alkynyleneheteroarylene.

Q is selected from a single bond and a multivalent group;

m is an integer equal to at least 2; and

p is 0 or 1.

In another embodiment, the present invention is directed to an electronic device having at least one active layer comprising a material

selected from Formulae I, II, and III, shown in Figures 1 through 3, wherein Ar¹, R¹ through R³, Q, a through d, m, n, p, x, and z are as defined above.

As used herein, the term "charge transport composition" is intended to mean material that can receive a charge from an electrode and facilitates movement through the thickness of the material with relatively high efficiency and small loss of charge. Hole transport compositions are capable of receiving a positive charge from an anode and transporting it. Electron transport compositions are capable of receiving a negative charge from a cathode and transporting it. The term "anti-quenching composition" is intended to mean a material which prevents, retards, or diminishes both the transfer of energy and the transfer of an electron to or from the excited state of the photoactive layer to an adjacent layer. The term "photoactive" refers to any material that exhibits electroluminescence, photoluminescence, and/or photosensitivity. The term "HOMO" refers to the highest occupied molecular orbital of a compound. The term "LUMO" refers to the lowest unoccupied molecular orbital of a compound. The term "group" is intended to mean a part of a compound, such as a substituent in an organic compound. The prefix "hetero" indicates that one or more carbon atoms has been replaced with a different atom. The term "alkyl" is intended to mean a group derived from an aliphatic hydrocarbon having one point of attachment, which group may be unsubstituted or substituted. The term "heteroalkyl" is intended to mean a group derived from an aliphatic hydrocarbon having at least one heteroatom and having one point of attachment, which group may be unsubstituted or substituted. The term "alkylene" is intended to mean a group derived from an aliphatic hydrocarbon and having two or more points of attachment. The term "heteroalkylene" is intended to mean a group derived from an aliphatic hydrocarbon having at least one heteroatom and having two or more points of attachment. The term "alkenyl" is intended to mean a group derived from a hydrocarbon having one or more carbon-carbon double bonds and having one point of attachment, which group may be unsubstituted or substituted. The term "alkynyl" is intended to mean a group derived from a hydrocarbon having one or more carbon-carbon triple bonds and having one point of attachment, which group may be unsubstituted or substituted. The term "alkenylene" is intended to mean a group derived from a hydrocarbon having one or more carbon-carbon double bonds and having two or more points of attachment, which group

may be unsubstituted or substituted. The term “alkynylene” is intended to mean a group derived from a hydrocarbon having one or more carbon-carbon triple bonds and having two or more points of attachment, which group may be unsubstituted or substituted. The terms “heteroalkenyl”, “heteroalkenylene”, “heteroalkynyl” and “heteroalkynylene” are intended to mean analogous groups having one or more heteroatoms. The term “aryl” is intended to mean a group derived from an aromatic hydrocarbon having one point of attachment, which group may be unsubstituted or substituted. The term “heteroaryl” is intended to mean a group derived from an aromatic group having at least one heteroatom and having one point of attachment, which group may be unsubstituted or substituted. The term “arylalkylene” is intended to mean a group derived from an alkyl group having an aryl substituent, which group may be further unsubstituted or substituted. The term “heteroarylalkylene” is intended to mean a group derived from an alkyl group having a heteroaryl substituent, which group may be further unsubstituted or substituted. The term “arylene” is intended to mean a group derived from an aromatic hydrocarbon having two points of attachment, which group may be unsubstituted or substituted. The term “heteroarylene” is intended to mean a group derived from an aromatic group having at least one heteroatom and having two points of attachment, which group may be unsubstituted or substituted. The term “arylenealkylene” is intended to mean a group having both aryl and alkyl groups and having one point of attachment on an aryl group and one point of attachment on an alkyl group. The term “heteroarylenealkylene” is intended to mean a group having both aryl and alkyl groups and having one point of attachment on an aryl group and one point of attachment on an alkyl group, and in which there is at least one heteroatom. Unless otherwise indicated, all groups can be unsubstituted or substituted. The phrase “adjacent to,” when used to refer to layers in a device, does not necessarily mean that one layer is immediately next to another layer. On the other hand, the phrase “adjacent R groups,” is used to refer to R groups that are next to each other in a chemical formula (i.e., R groups that are on atoms joined by a bond). The term “compound” is intended to mean an electrically uncharged substance made up of molecules that further consist of atoms, wherein the atoms cannot be separated by physical means. The term “ligand” is intended to mean a molecule, ion, or atom that is attached to the coordination sphere of a metallic ion. The term “complex”, when used as a noun, is intended to

mean a compound having at least one metallic ion and at least one ligand. The term "polymeric" is intended to encompass oligomeric species and include materials having 2 or more monomeric units. In addition, the IUPAC numbering system is used throughout, where the groups from the
5 Periodic Table are numbered from left to right as 1 through 18 (CRC Handbook of Chemistry and Physics, 81st Edition, 2000).

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Unless otherwise
10 defined, all letter symbols in the figures represent atoms with that atomic abbreviation. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references
15 mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent
20 from the following detailed description, and from the claims.

DESCRIPTION OF THE DRAWINGS

- Figure 1 shows Formula I for a charge transport composition of the invention.
- 25 Figure 2 shows Formula II for a charge transport composition of the invention.
- Figure 3 shows Formula III for a charge transport composition of the invention.
- Figure 4 shows Formulae I(a) through I(ag) for a charge transport
30 composition of the invention.
- Figure 5 shows Formulae IV(a) through IV(h) for a multidentate linking group.
- Figure 6 shows Formulae II(a) through II(l) for a charge transport composition of the invention.
- 35 Figure 7 shows Formulae V(a) through V(e) for electroluminescent iridium complexes.
- Figure 8 is a schematic diagram of a light-emitting diode (LED).
- Figure 9 is a schematic diagram of a testing device for an LED.

Figure 10 shows formulae for known electron transport compositions.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The quinoxaline derivative compounds represented by Formula I, shown in Figure 1, have particular utility as electron transport compositions and as anti-quenching agents. The quinoxaline compounds can also be used as hosts for light emitting materials.

In general, n is an integer. In one embodiment, n is an integer from 1 through 20. In one embodiment, n is an integer from 1 through 12.

10 In one embodiment, R^1 is selected from phenylalkenyl and phenylalkynyl groups, which may be further substituted.

In one embodiment, R^1 is selected from alkylacetate and arylcarbonyl groups, which may be further substituted.

15 In one embodiment, R^1 is selected from alkyl groups having 1 through 12 carbon atoms.

In one embodiment, R^2 is selected from phenyl groups, substituted phenyl groups, pyridyl groups, and substituted pyridyl groups. The substituent can be selected from F, Cl, Br, hydroxyl, carboxyl, carbonyl, silyl, siloxyl, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, 20 alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, $C_nH_aF_b$, $OC_nH_aF_b$, $C_6H_cF_d$, and $OC_6H_cF_d$.

In one embodiment, both of R^2 together are a biarylene group, which may be further substituted. In one embodiment, the biarylene group is selected from biphenylene and bipyridylene. The substituent can be 25 selected from F, Cl, Br, hydroxyl, carboxyl, carbonyl, silyl, siloxyl, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, $C_nH_aF_b$, $OC_nH_aF_b$, $C_6H_cF_d$, and $OC_6H_cF_d$.

30 Examples of suitable ET/AQ compounds of this type include, but are not limited to those given as Formulae I(a) through I(ag) in Figure 4.

The compositions represented by Formula I can be prepared using standard synthetic organic techniques, as illustrated in the examples. The compounds can be applied as thin films by evaporative techniques or conventional solution processing methods. As used herein, "solution 35 processing" refers to the formation of films from a liquid medium. The liquid medium can be in the form of a solution, a dispersion, an emulsion, or other forms. Typical solution processing techniques include, for

example, solution casting, drop casting, curtain casting, spin-coating, screen printing, inkjet printing, gravure printing, and the like.

In some cases it is desirable to increase the T_g of the compounds to improve stability, coatability, and other properties. This can be accomplished by linking together two or more of the compounds with a linking group to form compounds having Formula II, shown in Figure 2, or Formula III, shown in Figure 3. In these formulae, Q can be a single bond or a multivalent linking group, having two or more points of attachment. The multivalent linking group can be a hydrocarbon group with two or more points of attachment, and can be aliphatic or aromatic. The multivalent linking group can be a heteroalkylene or heteroarylene group, where the heteroatoms can be, for example, N, O, S, or Si. Examples of multivalent groups, Q, include, but are not limited to, alkylene, alkenylene, and alkynylene groups, and analogous compounds with heteroatoms; single, multiple-ring, and fused-ring aromatics and heteroaromatics; arylamines, such as triaryl amines; silanes and siloxanes. Additional examples of multivalent Q groups are given in Figure 5 as Formulae V(a) through V(h). In Formula IV(f), any of the carbons may be linked to a charge transport moiety. In Formula IV(h), any of the Si atoms can be linked to a charge transport moiety. Heteroatoms such as Ge and Sn can also be used. The linking group can also be $-\text{[SiMeR}^1\text{-SiMeR}^1\text{]}_n-$, where R^1 and n are as defined above.

In general, m is an integer equal to at least 2. The exact number depends on the number of available linking positions on Q and on the geometries of the quinoxaline moiety and Q. In one embodiment, m is an integer from 2 through 10.

In one embodiment, in Formula II, R^1 is selected from phenyl and substituted phenyl groups. The substituents can be selected from F, Cl, Br, alkyl, heteroalkyl, alkenyl, and alkynyl.

In one embodiment, in Formula II, R^1 is selected from alkylacetate and arylcarbonyl groups, which may be further substituted.

In one embodiment, in Formula II, R^1 is selected from alkyl groups having 1 through 12 carbon atoms.

In one embodiment, in Formula II, R^2 is selected from phenyl groups, substituted phenyl groups, pyridyl groups, and substituted pyridyl groups. The substituent can be selected from F, Cl, Br, hydroxyl, carboxyl, carbonyl, silyl, siloxyl, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl,

alkenylheteroaryl, alkynylheteroaryl, $C_nH_aF_b$, $OC_nH_aF_b$, $C_6H_cF_d$, and $OC_6H_cF_d$.

In one embodiment, in Formula II, both of R^2 together are a biarylene group, which may be further substituted. In one embodiment, the biarylene group is selected from biphenylene and bipyridylene. The substituent can be selected from F, Cl, Br, hydroxyl, carboxyl, carbonyl, silyl, siloxyl, alkyl, heteroalkyl, alkenyl, alkynyl, aryl, heteroaryl, alkylenearyl, alkenylaryl, alkynylaryl, alkyleneheteroaryl, alkenylheteroaryl, alkynylheteroaryl, $C_nH_aF_b$, $OC_nH_aF_b$, $C_6H_cF_d$, and $OC_6H_cF_d$.

In one embodiment, in Formula II, x is 0.

In one embodiment, in Formula II, R^3 is selected from aryl, heteroaryl, alkyl, and heteroalkyl. In one embodiment, in Formula II, R^3 is selected from phenyl and substituted phenyl. In one embodiment, in Formula II, R^3 is selected from alkyl and heteroalkyl having from 1 through 12 carbon atoms, which may be further substituted.

In one embodiment, in Formula III, R^1 is selected from phenylalkenyl and phenylalkynyl groups, which may be further substituted.

In one embodiment, in Formula III, R^1 is selected from alkylacetate and arylcarbonyl groups, which may be further substituted.

In one embodiment, in Formula III, R^1 is selected from alkyl groups having 1 through 12 carbon atoms.

In one embodiment in Formula III, R^2 is H.

In one embodiment in Formula III, R^3 is selected from aryl, heteroaryl, alkyl, and heteroalkyl. In one embodiment, in Formula III, R^3 is selected from phenyl and substituted phenyl. In one embodiment, in Formula III, R^3 is selected from alkyl and heteroalkyl having from 1 through 12 carbon atoms, which may be further substituted.

Specific examples of linked compounds having Formula II are given in Figure 6, Formulae II(a) through II(l).

Electronic Device

The present invention also relates to an electronic device comprising at least one of the charge transport compositions of the invention positioned between a photoactive layer and one electrode. A typical device structure is shown in Figure 8. The device 100 has an anode layer 110 and a cathode layer 160. Adjacent to the anode is a layer 120 comprising hole transport material. Adjacent to the cathode is a layer 140 comprising an electron transport and/or anti-quenching material ("ET/AQ"). Between the hole transport layer and the electron transport

and/or anti-quenching layer is the photoactive layer 130. As an option, devices frequently use another electron transport layer 150, next to the cathode. Layers 120, 130, 140, and 150 are individually and collectively referred to as the active layers.

5 Depending upon the application of the device 100, the photoactive layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector).
10 Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, and phototubes, and photovoltaic cells, as these terms are describe in Markus, John, *Electronics and Nucleonics Dictionary*, 470 and 476 (McGraw-Hill, Inc. 1966).

 The quinoxaline derivative compounds of the invention are
15 particularly useful as the electron transport and/or anti-quenching composition in layer 140, or as electron transport composition in layer 150. For example, in one embodiment, the quinoxaline derivative compounds of the invention may be used as the electron transport and/or anti-quenching layer in light emitting diode.

20 It is also to be understood that the ET/AQ material has to be chemically compatible with the photoactive material used. For example, the ET/AQ material has to form a smooth film when deposited on the photoactive material layer. If aggregation occurs, the performance of the device will deteriorate.

25 The other layers in the device can be made of any materials which are known to be useful in such layers. The anode 110, is an electrode that is particularly efficient for injecting positive charge carriers. It can be made of, for example materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide, or it can be a conducting polymer, and
30 mixtures thereof. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8-10 transition metals. If the anode is to be light-transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, are generally used. The anode 110 may also comprise an organic material such as polyaniline as described in
35 "Flexible light-emitting diodes made from soluble conducting polymer," *Nature* vol. 357, pp 477-479 (11 June 1992). At least one of the anode and cathode should be at least partially transparent to allow the generated light to be observed.

Examples of hole transport materials which may be used for layer 120 have been summarized, for example, in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837-860, 1996, by Y. Wang. Both hole transporting molecules and polymers can be used.

- 5 Commonly used hole transporting molecules are: N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA), a-phenyl-4-N,N-
- 10 diphenylaminostyrene (TPS), p-(diethylamino)benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB),
- 15 N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), and porphyrinic compounds, such as copper phthalocyanine. Commonly used hole transporting polymers are polyvinylcarbazole, (phenylmethyl)polysilane, and polyaniline and mixtures thereof. It is also possible to obtain hole transporting polymers by doping hole transporting
- 20 molecules such as those mentioned above into polymers such as polystyrene and polycarbonate.

- Examples of the photoactive layer 130 include all known electroluminescent materials. Organometallic electroluminescent compounds are preferred. The most preferred compounds include
- 25 cyclometalated iridium and platinum electroluminescent compounds and mixtures thereof. Complexes of Iridium with phenylpyridine, phenylquinoline, or phenylpyrimidine ligands have been disclosed as electroluminescent compounds in Petrov et al., Published PCT Application WO 02/02714. Other organometallic complexes have been described in,
- 30 for example, published applications US 2001/0019782, EP 1191612, WO 02/15645, and EP 1191614. Electroluminescent devices with an active layer of polyvinyl carbazole (PVK) doped with metallic complexes of iridium have been described by Burrows and Thompson in published PCT applications WO 00/70655 and WO 01/41512. Electroluminescent
- 35 emissive layers comprising a charge carrying host material and a phosphorescent platinum complex have been described by Thompson et al., in U.S. Patent 6,303,238, Bradley et al., in Synth. Met. (2001), 116 (1-3), 379-383, and Campbell et al., in Phys. Rev. B, Vol. 65 085210. as have

been Examples of a few suitable iridium complexes are given in Figure 7, as Formulae VI(a) through VI(e). Analogous tetradentate platinum complexes can also be used. These electroluminescent complexes can be used alone, or doped into charge-carrying hosts, as noted above. The quinoxaline materials of the present invention may also be used as such charge-carrying hosts in the emissive layer.

The cathode 160, is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode can be any metal or nonmetal having a lower work function than the anode. Materials for the cathode can be selected from alkali metals of Group 1 (e.g., Li, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, including the rare earth elements and lanthanides, and the actinides. Materials such as aluminum, indium, calcium, barium, samarium and magnesium, as well as combinations, can be used. Li-containing organometallic compounds, LiF, and Li₂O can also be deposited between the organic layer and the cathode layer to lower the operating voltage.

It is known to have other layers in organic electronic devices. For example, there can be a layer (not shown) between the anode 110 and hole transport layer 120 to facilitate positive charge transport and/or band-gap matching of the layers, or to function as a protective layer. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of anode layer 110, the hole transport layer 120, the electron transport layers 140 and 150, and cathode layer 160, may be surface treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers is preferably determined by balancing the goals of providing a device with high device efficiency with device operational lifetime.

It is understood that each functional layer may be made up of more than one layer.

The device can be prepared by a variety of techniques, including sequentially vapor depositing the individual layers on a suitable substrate. Substrates such as glass and polymeric films can be used. Conventional vapor deposition techniques can be used, such as thermal evaporation, chemical vapor deposition, and the like. Alternatively, the organic layers can be applied from solutions or dispersions in suitable solvents, using any conventional coating or printing technique, including but not limited to spin-coating, dip-coating, roll-to-roll techniques, ink-jet printing, screen

printing and gravure printing. In general, the different layers will have the following range of thicknesses: anode 110, 500-5000Å, preferably 1000-2000Å; hole transport layer 120, 50-2000Å, preferably 200-1000Å; photoactive layer 130, 10-2000 Å, preferably 100-1000Å; electron
5 transport layer 140 and 150, 50-2000Å, preferably 100-1000Å; cathode 160, 200-10000Å, preferably 300-5000Å. The location of the electron-hole recombination zone in the device, and thus the emission spectrum of the device, can be affected by the relative thickness of each layer. Thus the thickness of the electron-transport layer should be chosen so that the
10 electron-hole recombination zone is in the light-emitting layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used.

The quinoxaline derivative compounds of the invention may be useful in applications other than OLEDs. For example, these
15 compositions may be used in photovoltaic devices for solar energy conversion. They may also be used in field effect transistor for smart card and thin film transistor (TFT) display driver applications.

EXAMPLES

The following examples illustrate certain features and advantages
20 of the present invention. They are intended to be illustrative of the invention, but not limiting. All percentages are by weight, unless otherwise indicated.

EXAMPLES 1-16

These examples illustrate the preparation of quinoxaline derivative
25 ET/AQ compositions.

EXAMPLE 1

This example illustrates the preparation of Compound I(n) in Figure
4.

An oven-dried resealable Schlenk flask was charged with 2,3-(bi-4-
30 fluorophenyl)-6-bromoquinoxaline (2.00 g, 5.00 mmol), *para*-tert-butylstyrene (1.02 g, 6.40 mmol), Na₂CO₃ (0.68 g, 6.40 mmol), *trans*-di(μ-acetato)bis[o-(di-*o*-tolyl-phosphino)benzyl]dipalladium (II) (0.020 g, 0.02 mmol) and 2,6-di-tert-butyl-*p*-cresol (0.552 g, 2.50 mmol) and N,N-dimethylacetamide (12mL). The Schlenk flask was sealed with a Teflon
35 valve and the reaction mixture was heated at 130°C for 21 h. The resulting mixture was cooled to room temperature, diluted in Et₂O (230 mL) and filtered through a pad of silica. The filtrate was washed with water (2x100 mL) and brine (1x50 mL). The organic layer was dried and

concentrated to give a crude product which was then purified by flash chromatography to afford the pure product as a light-yellow solid in 72% (1.71 g) yield. ^{19}F NMR (376.8 Hz, CD_2Cl_2): δ -113.48 and -113.58.

EXAMPLE 2

5 This example illustrates the preparation of Compound I(o) in Figure 4.

 An oven-dried resealable Schlenk flask was charged with 4-fluorophenylacetylene (0.334 g, 2.78 mmol), 2,3-(bi-4-fluorophenyl)-6-bromoquinoxaline (1 g, 2.53 mmol), $\text{Pd}_2(\text{dba})_3$ (0.046 g, 0.05 mmol),
10 triphenylphosphine (0.066 g, 0.253 mmol), CuI (0.010 g, 0.05 mmol) and triethylamine (15 mL). The flask was then sealed and heated at 60°C for 24 hours. The reaction mixture was diluted with CH_2Cl_2 , washed with H_2O and brine, dried over MgSO_4 , filtered and concentrated to afford an off-white solid. The crude product was purified by repeated washes with
15 hexanes (3x20 mL) to yield 0.924 g (84% yield). ^1H NMR (CD_2Cl_2 , 500 MHz) δ 8.37 (d, 1H, $J=1.6$), 8.20-8.18 (d, 1H, 8.8), 7.98-7.95 (dd, 1H, $J=8.3$, 1.5), 7.74-7.70 (dd, 2H, $J=5.4$, 3.6), 7.64-7.60 (m, 4H), 7.24-7.14 (m, 6H). ^{19}F NMR (CD_2Cl_2 , 500 MHz) δ -111.14 (m, 1F), -113.1 (m, 2F).

EXAMPLE 3

20 This example illustrates the preparation of Compound I(q) in Figure 4.

 A reactor was charged with Compound I(n) from Example 1 (1.70g, 3.55 mmol), ESCAT 140 Pd/C catalyst (0.056 g), and MeOH (45 mL). The reaction mixture was flushed with nitrogen, pressurized to 500 psig H_2 and
25 heated up to 60 C for 8h. The volatiles were removed under vacuum and the product was purified by flash chromatography (5%EtOAc/hexane, where "Et" represents ethyl and "OAc" represents acetate) to yield a light-yellow powder (0.220 g, 13%). ^{19}F NMR (376.8 Hz, CD_2Cl_2): δ -111.14 and -114.60.

EXAMPLE 4

30 This example illustrates the preparation of Compound I(b) in Figure 4.

 A mixture of 3,4-diaminotoluene (28.78 g, .236 mol) and benzil (45 g, .214 mol) was refluxed in 738 mL chloroform with 2.16 mL trifluoroacetic acid for 3 hours. The mixture was washed 3 times with 10% HCl, brine, and
35 dried over MgSO_4 , filtered, and then filtered through a silica bed with vacuum. The resultant solution was evaporated to dryness. Recrystallized 69 grams of crude product from 550 mL methanol. Filtered solids were

dried in a vacuum oven at 50°C for 1 hour to yield 55.56 g of dried solid.
78.8% yield

EXAMPLE 5

5 This example illustrates the preparation of Compound I(e) in Figure
4.

A mixture of 3,4-diaminotoluene (4.49 g, .037 mol) and 4,4'-
dimethoxybenzil (9.46g, .035 mol) was refluxed in 125 mL chloroform with
0.35 mL trifluoroacetic acid for 6 hours. The mixture was washed 2 times
10 with water, dried over MgSO₄, and evaporated to ~11g. The solid was
dissolved in 1:1 ethyl acetate : chloroform for flash chromatography and
eluted with ethyl acetate. Evaporated to 9.7 grams of dark solid. 72% yield

EXAMPLE 6

15 This example illustrates the preparation of Compound I(c) in Figure
4.

A mixture of 3,4-diaminotoluene (0.603 g, 4.93 mmol) and 1,10-
phenanthroline-5,6-dione (0.945g, 4.50 mmol) was refluxed in 602 mL
chloroform with 0.35 mL trifluoroacetic acid for 6 hours. The mixture was
filtered hot through a medium frit to yield 0.85 g of light yellow solid after
20 drying. Yield 63%

A second crop was obtained from mother liquor after cooling to yield an
additional 0.31 g.

EXAMPLE 7

25 This example illustrates the preparation of Compound I(d) in Figure
4.

A mixture of 3,4-diaminotoluene (5.36 g, 44 mmol) and
phenanthrene quinone (8.33g, .040 mol) was refluxed in 119 mL
chloroform with 0.4 mL trifluoroacetic acid for 6 hours. The mixture was
filtered through a medium frit and recrystallized from 430 g of methyl ethyl
30 ketone to yield 5.5 g fluffy wool-like, yellow product. 46% yield

EXAMPLE 8

This example illustrates the preparation of Compound I(f) in Figure
4.

35 A mixture of 3,4-diaminotoluene (5.36 g, 44 mmol) and 2,2'-Pyridil
(8.49 g, 40 mmol) was refluxed in 119 mL chloroform with 0.4 mL
trifluoroacetic acid for 4 hours. The reaction mixture was separated and
washed 4 times with 100 mL water, and evaporated to 10.4 g. The
resultant solid was dissolved in 1:1 ethyl acetate:chloroform for flash

chromatography and eluted with ethyl acetate. Evaporated to yield 9.3g of solid.

EXAMPLE 9

This example illustrates the preparation of Compound I(g) in Figure

5 4.

A mixture of methyl-3,4-diaminobenzoate (7.28 g, 44 mmol) and benzil (8.41 g, 40 mmol) was refluxed in 140 ml methylene chloride for 21 hours. The reaction mixture was evaporated to dryness and then dissolved in 520 mL methanol and 150 mL methylene chloride at reflux. The solution
10 was then partially evaporated to selectively crystallize the desired product

EXAMPLE 10

This example illustrates the preparation of Compound I(k) in Figure

4.

A mixture of Methyl-3,4-diaminobenzoate (6.37 g, .038 mol) and
15 4,4'-dimethoxybenzil (9.46g, .035 mol) was refluxed in 142 mL methylene chloride with 3 drops trifluoroacetic acid for 5 hours. 10.7g N-methylpyrrolidinone was added and reflux continued for 26 more hours. The mixture was washed 3 times with water, dried over MgSO₄, filtered and then precipitated the product by decanting the organic solution into
20 550 g methanol. After standing overnight, the product was filtered and dried at 95°C in vacuum to yield 10.39g product.

EXAMPLE 11

This example illustrates the preparation of Compound I(r) in Figure

4.

A mixture of Methyl-3,4-diaminobenzoate (6.12 g, .037 mol) and
25 phenanthrene quinone (7.08g, .034 mol) was refluxed in 119 mL methylene chloride. 100 g of N-methylpyrrolidinone was added and the chlorinated solvent was distilled out. The pot was warmed to 150°C whereupon a clear solution was obtained and the reaction was tracked by
30 gas chromatography. The product was precipitated by pouring into 410 g methanol and the solid precipitate filtered off. The product was recrystallized from toluene then recrystallized again from a combination of methyl ethyl ketone 1200 g, toluene 150 g, and tetrahydrofuran 1100 g. Yield was 3.3 g of pearly golden wool-like material.

35

EXAMPLE 12

This example illustrates the preparation of Compound I(l) in Figure

4.

A mixture of 1,2-phenylenediamine (13.91 g, 0.129 mol) and 4,4'-

dibromobenzil (45g, 0.116 mol) was refluxed in 558 mL chloroform with 1.0 ml trifluoroacetic acid for 6 hours. The mixture was washed 3 times with 10% HCl, and evaporated to ~51 g. Recrystallized from 600 mL ethyl acetate with 100mL methanol at reflux. Large crystals formed overnight
5 and were filtered and washed with methanol twice and dried to 29.63g with a 4.9 g second crop from the chilled mother liquor.

EXAMPLE 13

This example illustrates the preparation of Compound I(h) in Figure
4.

10 A mixture of 2,3-diaminotoluene (4.84 g, .040 mol) and benzil (7.56 g, 0.036 mol) was refluxed in 112 mL methylene chloride for 19 hours. The mixture was washed 4 times with 12% HCl, and dried over MgSO₄ filtered and evaporated to ~9.5 g of brown solid. The solid was
15 distilled out. Cooling with ice yielded nice crystals. Filtered and washed crystal cake with methanol.

EXAMPLE 14

This example illustrates the preparation of Compound I(i) in Figure
4.

20 A mixture of 2,3-diaminotoluene (5.05 g, 0.041 mol) and phenanthrenequinone (7.84 g, .0.038 mol) were refluxed in 112 ml chloroform for 29 hours. The resultant solution was chromatographed down a silica column with chloroform eluant. Evaporated product from solvent to yield about 10 g before vacuum oven drying. Material appeared
25 crystalline

EXAMPLE 15

This example illustrates the preparation of Compound I(j) in Figure
4.

30 A mixture of methyl-3,4-diaminobenzoate (7.28 g 0.044 mol) and 2,2'-pyridil (8.48 g, 0.040 mol) was refluxed in 140 mL methylene chloride for 7 hours. The solution was evaporated to 15.7 g and the solid dissolved in 240 mL methylene chloride and 140 mL methanol at reflux. After addition of 280 mL methanol and evaporation of ~150 mL of the solvent the solution was left to stand overnight. The resulting solid was collected
35 and dried to 9.8 g. Took 7.7 g material and dissolved in 203 g methanol with 50 g methylene chloride. Distilled off > 50 mL of solvent. Crystals formed overnight. Filtered and dried in vacuum oven.

EXAMPLE 16

This example illustrates the preparation of Compound I(t) in Figure 4.

An oven-dried resealable Schlenk flask was charged with 2,3-(bi-4-fluorophenyl)-6-bromoquinoxaline (1.23 g, 3.08 mmol), 1,3-divinyltetramethyldisiloxane (3.40 mL, 14.8 mmol), KOAc (0.440 g, 4.48 mmol), Pd(OAc)₂ (0.012 g, 0.06 mmol), P(o-Tol)₃ (0.06g, 0.20 mmol), NEt₃ (0.300 mL), DMF (~2 mL) and water (0.45mL). The Schlenk flask was sealed with a Teflon valve and the reaction mixture was heated at 95°C for 48 h. The resulting mixture was cooled to room temperature, diluted in water (15 mL) and the product was extracted with CH₂Cl₂ (15 mL). The organic layer was dried and concentrated to give a crude product, which was purified by chromatography (3% EtOAc/hexane) as a light-yellow solid (0.478 g, 31% yield). ¹⁹F NMR (376.8 Hz, CD₂Cl₂): δ – 113.45 (br m).

EXAMPLES 17-19

These examples illustrate the preparation of charge transport compositions having more than one quinoxaline group.

EXAMPLE 17

This example illustrates the preparation of Compound II(e) in Figure 6.

A 3-necked 500 mL round bottomed flask fitted with a nitrogen inlet and a condensor was charged with 1,4-phenylenebisboronic acid (2 g, 12.1 mmol), 2,3-(bi-4-fluorophenyl)-6-bromoquinoxaline (9.54 g, 24.1 mmol), Pd(PPh₃)₄ (2.78 g, 2.41 mmol), potassium carbonate (6.67 g, 48.3 mmol), DME (150 mL) and H₂O (150 mL). The reaction mixture was refluxed for 24 h, after which it was diluted with H₂O and CH₂Cl₂. The organic layer contained a precipitate, which was isolated by filtration and washed with CH₂Cl₂ to yield 2.75 g (32% yield) of an off-white powder. ¹H NMR (CD₂Cl₂, 500 MHz) δ 8.56-8.55 (m, 2H), 8.35-8.33 (d, 2H), 8.29 (m, 2H), 8.12 (s, 4H), 7.68-7.64 (m, 8H), 7.29-7.16 (m, 8H). ¹⁹F NMR (CD₂Cl₂, 500 MHz) δ -113.35 (m, 2F).

EXAMPLE 18

This example illustrates the preparation of Compound II(k) in Figure 6.

A mixture of 1,4-bisbenzil (1 g, 2.92 mmol) and 4,5-dimethyl-1,2-phenylenediamine (0.769 g, 5.84 mmol) in chloroform (20 mL) was refluxed for 15 hrs under an atmosphere of nitrogen. Hexanes was added

to reaction mixture, precipitating out a bright yellow precipitate which was isolated by filtration and washed with hexanes to yield the product as a bright-yellow powder (1.32 g, 83% yield). ¹H NMR (CD₂Cl₂, 500 MHz) δ 7.89-7.88 (d, 4H, J=7.1 Hz), 7.50-7.48 (dd, 4H, J=1.5 Hz, 7.7 Hz), 7.45 (s, 4H), 7.35-7.31 (m, 10H), 2.53 (s, 12H).

EXAMPLE 19

This example illustrates the preparation of Compound II(a) in Figure 6.

A mixture of 3,3-diaminobenzidine (0.4580 g, 2.14 mmol) and 1,10-phenanthroline-5,6-dione (0.9458 g, 4.5 mmol) was heated at 85°C in 10 g N-methylpyrrolidinone with 0.045 ml trifluoroacetic acid for 23 hours. At ambient temperature chloroform was charged to the pot and the contents were filtered through a fine frit and washed with acetone, and diethylether then dried at 90°C and vacuum.

EXAMPLE 20

This example illustrates the preparation of Compound I(m) in Figure 4.

The synthesis of this compound was carried out following the synthetic method used for the preparation of I(o) to give the desired product in 58% yield. ¹H NMR (CD₂Cl₂, 500 MHz) δ 8.38 (d, 1H, J=1.8Hz), 8.20-8.18 (d, 1H, 8.4Hz), 7.99-7.97 (dd, 1H, J=1.8 Hz, 8.7Hz), 7.73-7.71 (m, 2H), 7.64-7.61 (m, 4H), 7.52-7.50 (m, 3H), 7.19-7.14 (m, 4H). ¹⁹F NMR (CD₂Cl₂, 500 MHz) δ-113.14 (m, 2F).

EXAMPLE 21

This example illustrates the preparation of Compound II(g) in Figure 6.

The synthesis of this compound was carried out following the synthetic method used for the preparation of II(e) to give the desired product in 13% yield. ¹H NMR (CD₂Cl₂, 500 MHz) δ 8.42-8.41 (d, 2H, J=1.9), 8.20-8.18 (d, 2H, J=8.5), 8.13-8.11 (dd, 2H, J=9.1 Hz, 2.0 Hz), 8.00 (s, 4H), 7.54-7.51 (dd, 8H, J=8.7 Hz, 3.1 Hz), 6.9-6.9 (q, 8H), 5.48 (s, 12H).

EXAMPLE 22

This example illustrates the preparation of Compound II(d) in Figure 6.

The synthesis of this compound was carried out following the synthetic method used for the preparation of II(e) to give the desired product in 10% yield. ¹H NMR (CD₂Cl₂, 500 MHz) δ 8.62-8.61 (d, 2H,

J=1.5), 8.44-8.41 (m, 4H), 8.41-8.39 (d, 2H, J=9.5 Hz), 8.34-8.31 (dd, 2H, J=8.3 Hz, 1.6 Hz), 8.14 (m, 6H), 8.12-8.11 (m, 2H), 7.98-7.94 (m, 4H), 7.38-7.34 (m, 4H).

EXAMPLE 23

5 This example illustrates the preparation of Compound II(k) in Figure 6.

The synthesis of this compound was carried out following the synthetic method used for the preparation of II(j) to give the desired product in 66% yield. ¹H NMR (CD₂Cl₂, 500 MHz) δ 8.09-8.06 (t, 2H, J=7.4 Hz), 7.98-7.96 (d, 2H, J=7.2 Hz), 7.69-7.67 (d, 2H, 8.9), 7.59-7.51 (m, 10H), 7.43-7.40 (m, 8H), 2.67 (s, 6H).

EXAMPLE 24

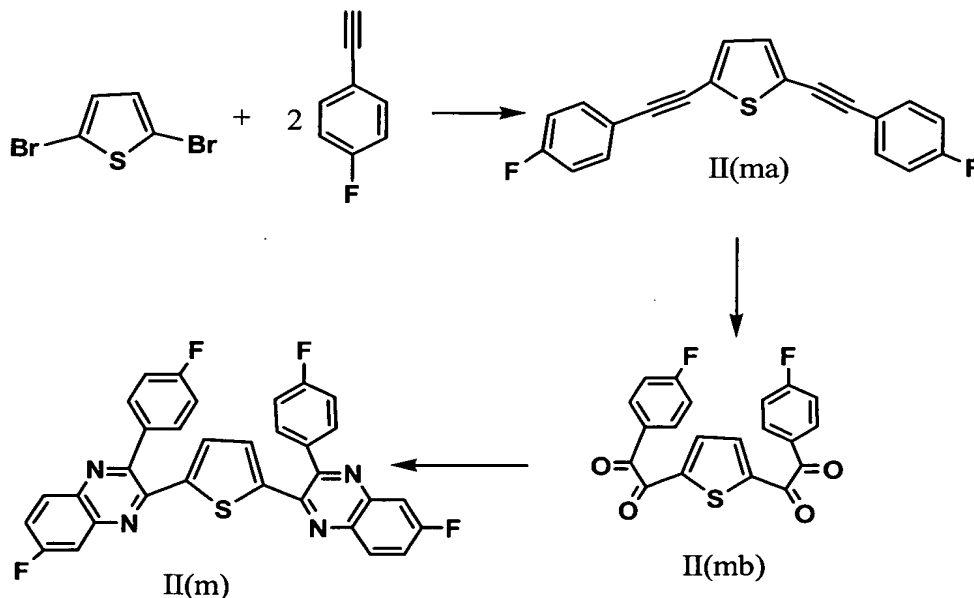
This example illustrates the preparation of Compound II(l) in Figure 6.

15 The synthesis of this compound was carried out following the synthetic method used for the preparation of II(j) to give the desired product in 65% yield. ¹H NMR (CD₂Cl₂, 500 MHz) δ 8.29-8.24 (m, 1H), 8.07-8.01 (m, 1H), 7.90-7.86 (m, 1H), 7.80-7.78 (m, 0.6H), 7.72-7.66 (m, 1H), 7.64-7.59 (m, 4H), 7.51-7.44 (m, 3H). ¹⁹F NMR (CD₂Cl₂, 500 MHz) δ -108.4 (m, 2F), -108.9 (m, 3F), -109.2 (m, 8F), -109.4 (m, 8F).

EXAMPLE 25

20 This example illustrates the preparation of Compound II(m) in Figure 6.

The synthesis of this compound was carried out using the synthetic scheme shown below.



Compound II(ma) was obtained using the synthetic method used for I(o) to produce the expected product in 65% yield. ^1H NMR (CD_2Cl_2 , 500 MHz) δ 7.64-7.60 (m, 4H), 7.27 (s, 2H), 7.20-7.16 (t, 4H, $J=8.9$ Hz). ^{19}F NMR (CD_2Cl_2 , 500 MHz) δ -111.10 (m, 2F). Under nitrogen, a three-necked round bottomed flask fitted with a condensor was charged with II(ma) (2.00 g, 6.25 mmol, 0.1 equiv.), Adogen 464 (0.125 g), potassium permanganate (4.9 g, 31.25 mmol, 5.00 equiv.), sodium bicarbonate (1.05 g, 12.5 mmol, 2.0 equiv.), H_2O (80 mL) and CH_2Cl_2 (50 mL). The mixture was allowed to reflux for 36 hours. After cooling to room temperature, 9.3 g sodium bicarbonate and 4 mL HCl were slowly added to the reaction mixture to neutralize and remove any excess oxidizing agents. The reaction mixture was then diluted with dichloromethane and H_2O , the layers separated and the organic portion washed with H_2O , brine and dried over MgSO_4 . The product was isolated by evaporating the solvent and then was recrystallized from ethanol to give 0.6 g (25% yield) of II(mb) as yellow needle-like crystals. ^1H NMR (CD_2Cl_2 , 500 MHz): δ 8.25-8.21 (dd, 4H, $J=8.9$ Hz, 5.6 Hz), 7.98 (s, 2H), 7.36-7.32 (t, 4H, $J=8.70$ Hz). ^{19}F NMR (CD_2Cl_2 , 500 MHz): δ -101.8 (m, 2F). The synthesis of compound II(m) was carried out following the procedure used for the preparation of II(k) to give the desired product in 20% yield. ^1H NMR (CD_2Cl_2 , 500 MHz) δ 8.25-8.21 (m, 1H), 8.19-8.15 (m, 1H), 7.85-7.78 (m, 2H), 7.73-7.64 (m, 6H), 7.29-7.25 (t, 4H), 6.69-6.66 (m, 2H). ^{19}F NMR (CD_2Cl_2 500 MHz) δ -108.7, -108.8 (m, 2F), -112.4 (m, 1F), -112.6 (m, 1F).

The properties of the electron transport and/or anti-quenching compositions are summarized in Table 1 below.

Table 1				
Properties				
Compounds	Absorption onset (nm), E1-E5	Absorption maximum (nm)	$E_{1/2}$ vs SCE (volt),	LUMO vs vacuum (eV), E1
Compound I(a)	375	345	-1.5	-3.33
Compound I(b)	378	339	-1.6	-3.24
Compound I(c)	400	385	-1.17	-3.67

Compound I(d)	410	397	-1.3	-3.54
Compound I(g)	390	352	-1.29	-3.55
Compound II(a)	--	--	--	--what is the purpose of this line?
Compound I(e)	405	369	-1.66	-3.18
Compound I(f)	378	339	-1.53	-3.31
Compound I(o)	420	382	-1.35	-3.49
Compound I(l)	407	394	-1.28	-3.56
Compound I(k)	385	343	-1.59	-3.25
Compound I(w)	417	401	-1.03	-3.81
Compound I(p)	380	347	-1.49	-3.35
Compound I(x)	380	342	-1.22	-3.62
Comp. A DDPA	368	310	-1.85	-2.99
Comp. B DPA	366	316	-1.95	-2.89

EXAMPLE 27

This example illustrates the preparation of an iridium electroluminescent complex, shown as Formula V(a) in Figure 7.

5 Phenylpyridine ligand, 2-(4-fluorophenyl)-5-trifluoromethylpyridine

The general procedure used was described in O. Lohse, P. Thevenin, E. Waldvogel *Synlett*, 1999, 45-48. A mixture of 200 ml of degassed water, 20 g of potassium carbonate, 150 ml of 1,2-dimethoxyethane, 0.5 g of Pd(PPh₃)₄, 0.05 mol of 2-chloro-5-trifluoromethylpyridine and 0.05 mol of 4-fluorophenylboronic acid was
10 refluxed (80-90°C) for 16-30 h. The resulting reaction mixture was diluted

with 300 ml of water and extracted with CH₂Cl₂ (2 x 100 ml). The combined organic layers were dried over MgSO₄, and the solvent removed by vacuum. The liquid products were purified by fractional vacuum distillation. The solid materials were recrystallized from hexane.

5 The typical purity of isolated materials was >98%.

Iridium complex:

A mixture of IrCl₃·nH₂O (54% Ir; 508 mg), 2-(4-fluorophenyl)-5-trifluoromethylpyridine, from above (2.20 g), AgOCOCF₃ (1.01 g), and water (1 mL) was vigorously stirred under a flow of N₂ as the temperature
10 was slowly (30 min) brought up to 185°C (oil bath). After 2 hours at 185-190°C the mixture solidified. The mixture was cooled down to room temperature. The solids were extracted with dichloromethane until the extracts decolorized. The combined dichloromethane solutions were filtered through a short silica column and evaporated. After methanol
15 (50 mL) was added to the residue the flask was kept at -10°C overnight. The yellow precipitate of the tris-cyclometalated complex, compound V(a) in figure 7A, was separated, washed with methanol, and dried under vacuum. Yield: 1.07 g (82%). X-Ray quality crystals of the complex were obtained by slowly cooling its warm solution in 1,2-dichloroethane.

20 EXAMPLE 28

This example illustrates the formation of OLEDs using the charge transport compositions of the invention.

Thin film OLED devices including a hole transport layer (HT layer), electroluminescent layer (EL layer) and at least one electron transport
25 and/or anti-quenching layer (ET/AQ layer) were fabricated by the thermal evaporation technique. An Edward Auto 306 evaporator with oil diffusion pump was used. The base vacuum for all of the thin film deposition was in the range of 10⁻⁶ torr. The deposition chamber was capable of depositing five different films without the need to break up the vacuum.

30 Patterned indium tin oxide (ITO) coated glass substrates from Thin Film Devices, Inc was used. These ITO's are based on Corning 1737 glass coated with 1400Å ITO coating, with sheet resistance of 30 ohms/square and 80% light transmission. The patterned ITO substrates were then cleaned ultrasonically in aqueous detergent solution. The
35 substrates were then rinsed with distilled water, followed by isopropanol, and then degreased in toluene vapor for ~3 hours.

The cleaned, patterned ITO substrate was then loaded into the vacuum chamber and the chamber was pumped down to 10⁻⁶ torr. The

substrate was then further cleaned using an oxygen plasma for about 5-10 minutes. After cleaning, multiple layers of thin films were then deposited sequentially onto the substrate by thermal evaporation. Finally, patterned metal electrodes of Al or LiF and Al were deposited through a mask. The thickness of the film was measured during deposition using a quartz crystal monitor (Sycon STC-200). All film thickness reported in the Examples are nominal, calculated assuming the density of the material deposited to be one. The completed OLED device was then taken out of the vacuum chamber and characterized immediately without encapsulation.

Table 2 summarizes the devices made with the quinoxaline derivative ET/AQ compositions of the invention. In all cases the anode was ITO, as discussed above, the hole transport layer was MPMP, and the emitting layer was the iridium complex from Example 27, having the thicknesses indicated. When present, electron transport layer 150 was tris(8-hydroxyquinolato)aluminum(III), Alq, having the thicknesses given. The cathode was a layer of Al or a dual layer of LiF/Al, with the thicknesses given.

TABLE 2					
Devices					
Sample	HT (Å)	EL, Å	ET/AQ, Å	ET, Å	Cathode, Å
Comparative A	507	407	Comp. A 408		Al 721
Comparative B	507	405	Comp. B 407		Al 732
3-1	545	403	I(a) 430	Alq 430	Al 737
3-2	508	625	I(b) 425		Al 732
3-3	509	413	I(c) 416		Al 750
3-4	578	411	I(d) 381		Al 711
3-5	527	418	I(e) 418		Al 1027

3-6	535	415	I(f) 459		AI 1039
3-7	549	425	I(g) 423		AI 1023
3-8	510	445	II(a) 415		AI 710
3-9	502	403	I(f) 106	Alq 303	LiF 5 AI 470
3-10	502	402	I(d) 102	Alq 303	LiF 5 AI 497
3-11	501	402	I(c) 103	Alq 302	LiF 5 AI 111
3-12	513	409	I(h) 414		AI 718
3-13	514	416	I(i) 408		AI 718
3-14	515	500	I(i) 410		AI 729
3-15	504	488	I(j) 402		AI 721
3-16	505	412	I(k) 439		AI 727
3-17	516	409	I(l) 432		AI 733
3-18	302	403	II(c) 102	Alq 302	LiF 10 AI 452
3-19	304	402	II(d) 101	Alq 302	LiF 10 AI 452
3-20	305	404	II(e) 102	Alq 303	LiF 10 AI 454
3-21	301	402	II(f) 105	Alq 305	LiF 10 AI 451
3-22	303	406	I(m) 103	Alq 302	LiF 10 AI 453
3-23	303	405	II(g) 102	Alq 305	LiF 10 AI 453
3-24	304	402	I(n) 101	Alq 303	LiF 10 AI 453

3-25	303	410	Il(h) 102	Alq 305	LiF 10 Al 453
3-26	306	404	I(o) 103	Alq 302	LiF 10 Al 453
3-27	305	404	Il(i) 192	Alq 305	LiF 10 Al 453
3-28	303	402	I(p) 102	Alq 304	LiF 10 Al 456
3-29	303	403	Il(j) 103	Alq 303	LiF 10 Al 335
3-30	303	405	Il(k) 102	Alq 305	LiF 10 Al 284
3-31	303	405	Il(l) 102	Alq 303	LiF 10 Al 232

The OLED samples were characterized by measuring their (1) current-voltage (I-V) curves, (2) electroluminescence radiance versus voltage, and (3) electroluminescence spectra versus voltage. The apparatus used, 200, is shown in Figure 9. The I-V curves of an OLED sample, 220, were measured with a Keithley Source-Measurement Unit Model 237, 280. The electroluminescence radiance (in the unit of cd/m^2) vs. voltage was measured with a Minolta LS-110 luminescence meter, 210, while the voltage was scanned using the Keithley SMU. The electroluminescence spectrum was obtained by collecting light using a pair of lenses, 230, through an electronic shutter, 240, dispersed through a spectrograph, 250, and then measured with a diode array detector, 260. All three measurements were performed at the same time and controlled by a computer, 270. The efficiency of the device at certain voltage is determined by dividing the electroluminescence radiance of the LED by the current density needed to run the device. The unit is in cd/A .

The results for devices using the quinoxaline derivative ET/AQ compositions of the invention are given in Table 3 below:

TABLE 3 Electroluminescent Properties of Devices				
<u>Sample</u>	Peak Radiance, cd/m ²	Efficiency at Peak Radiance cd/A	Peak efficiency, cd/A	Peak power efficiency lm/W
Comp. F	3000 at 22 V	10	14	
Comp. G	4500 at 19 V	10	20	
3-1	2300 at 20 V	4	5.4	
3-2	2700 at 27 V		10	
3-3	4000 at 15 V		10-16	
3-4	90 at 22 V		4.4	
3-5	200 at 22 V		1.1	
3-6	2500 at 21 V		8.5	
3-7	2000 at 22 V		13	
3-8	290 at 16 V		1.8	
3-9	7000 at 15 V		30	15
3-10	1000 at 25 V		14	
3-11	6500 at 15 V		26	
3-12	1200 at 20 V		9.5	
3-13	300 at 19 V		2.6	
3-14	220 at 26 V		2.6	

TABLE 3 Electroluminescent Properties of Devices				
<u>Sample</u>	Peak Radiance, cd/m ²	Efficiency at Peak Radiance cd/A	Peak efficiency, cd/A	Peak power efficiency lm/W
3-15	180 at 25 V		8.5	
3-16	1600 at 22 V		11	
3-17	100 at 22 V		1.2	
3-18	4200-5800 at 15 V		16-20	
3-19	4000-5000 at 15 V		17-20	
3-20	4800-5400 at 17 V		15-17	
3-21	2300 at 20 V		10.5	
3-22	4000 at 17 V		15-19 at 13 V	
3-23	5000 at 17 V		17-22 at 13 V	
3-24	5600 at 17 V		22 at 14 V	
3-25	1400 at 17 V		5.5 at 13 V	
3-26	8000 at 14 V		20 at 11 V	
3-27	7000 at 17 V		16 at 14 V	
3-28	6000 at 15 V		15-20 at 14-11 V	
3-29	6500 at 16 V		18 at 13 V	
3-30	6500 at 15 V		19 at 11 V	

<u>TABLE 3</u> Electroluminescent Properties of Devices				
<u>Sample</u>	Peak Radiance, cd/m ²	Efficiency at Peak Radiance cd/A	Peak efficiency, cd/A	Peak power efficiency lm/W
3-31	6000 at 16 V		14 at 12 V	